

BEST AVAILABLE COPY

(12) UK Patent Application (19) GB (11) 2 224 751 (13) A

(43) Date of A publication 16.05.1990

(21) Application No 8821453.1

(22) Date of filing 13.09.1988

(71) Applicant
Aican International Limited

(Incorporated in Canada - Quebec)

1188 Sherbrooke Street West, Montreal, Quebec,
H3A 3G2, Canada

(72) Inventors
Robert Anderson Ross
Rejean Lemay

(74) Agent and/or Address for Service
Stevens Hewlett and Perkins
5 Quality Court, Chancery Lane, London,
WC2A 1HZ, United Kingdom

(51) INT CL⁴
B23K 35/363, C23C 22/34 26/00

(52) UK CL (Edition J)
C7F FHD FP811 FP841 FR833 FR842 FR851 FR863
FR885 FR905 FXA F802 F809
B3R RPP R71469
C7M M205 M208 M22Y M225 M228 M30Y M305
M308 M47X M470 M475 M752 M753 M774 M775
M780 M782
U1S S1381 S1673

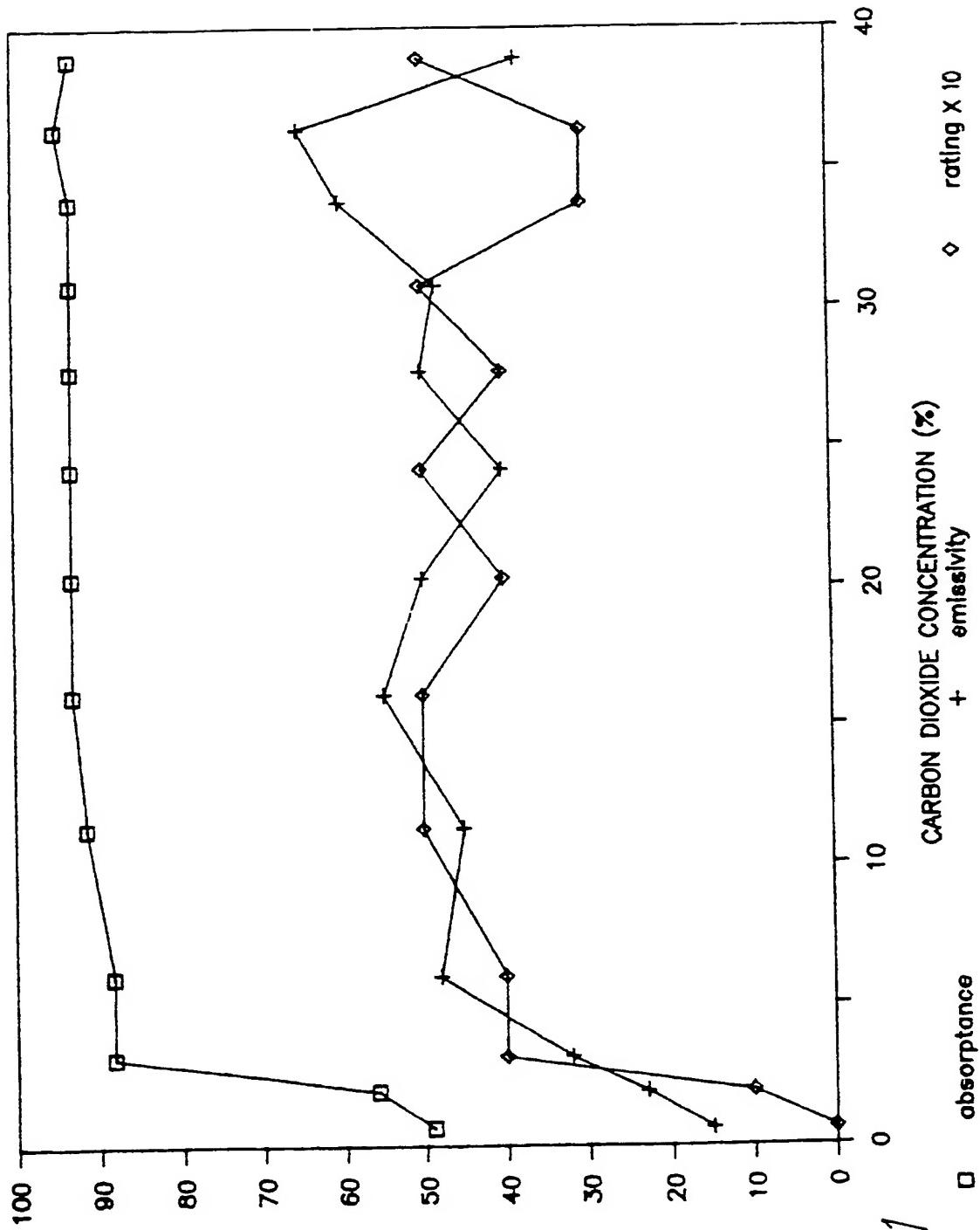
(56) Documents cited
GB 1134543 A GB 0783446 A GB 0750928 A
GB 0735698 A FR 1009090 A US 4723597 A
US 4655385 A US 3951328 A US 3149007 A
JP 62224496 A

(58) Field of search
UK CL (Edition J) C7F FHD FHZ FXA, C7M, C7U
INT CL⁴ B23K, C23C
Online databases: WPI

(54) Darkening aluminium workpieces; brazing

(57) A method of treating an aluminium workpiece which may be a heat exchanger to darken a surface thereof comprises applying a coating comprising alkali metal and halogen values to the surface, heating the coated workpiece in an inert atmosphere and bringing the heated workpiece into contact with a carbon oxide such as carbon dioxide. Alternatively the carbon oxide may be provided from a carbon-oxygen containing compound present in the coating, eg a carbohydrate such as sugars, starches, cellulose and their derivates; oxalates; or carbonates. The coating may be a brazing flux, such as that used in the Nocolok brazing systems such as a potassium/aluminium fluoride brazing flux and the method may be performed in conjunction with brazing. The aluminium workpiece which may be an alloy so treated has a blank adherent coating comprising potassium, fluorine, aluminium, carbon and oxygen values. The workpiece may be maintained in contact with the carbon oxide at a temperature of from 95% of the solidus temperature of the coating expressed in °K up to the solidus temperature of the workpiece, eg 560-640°C.

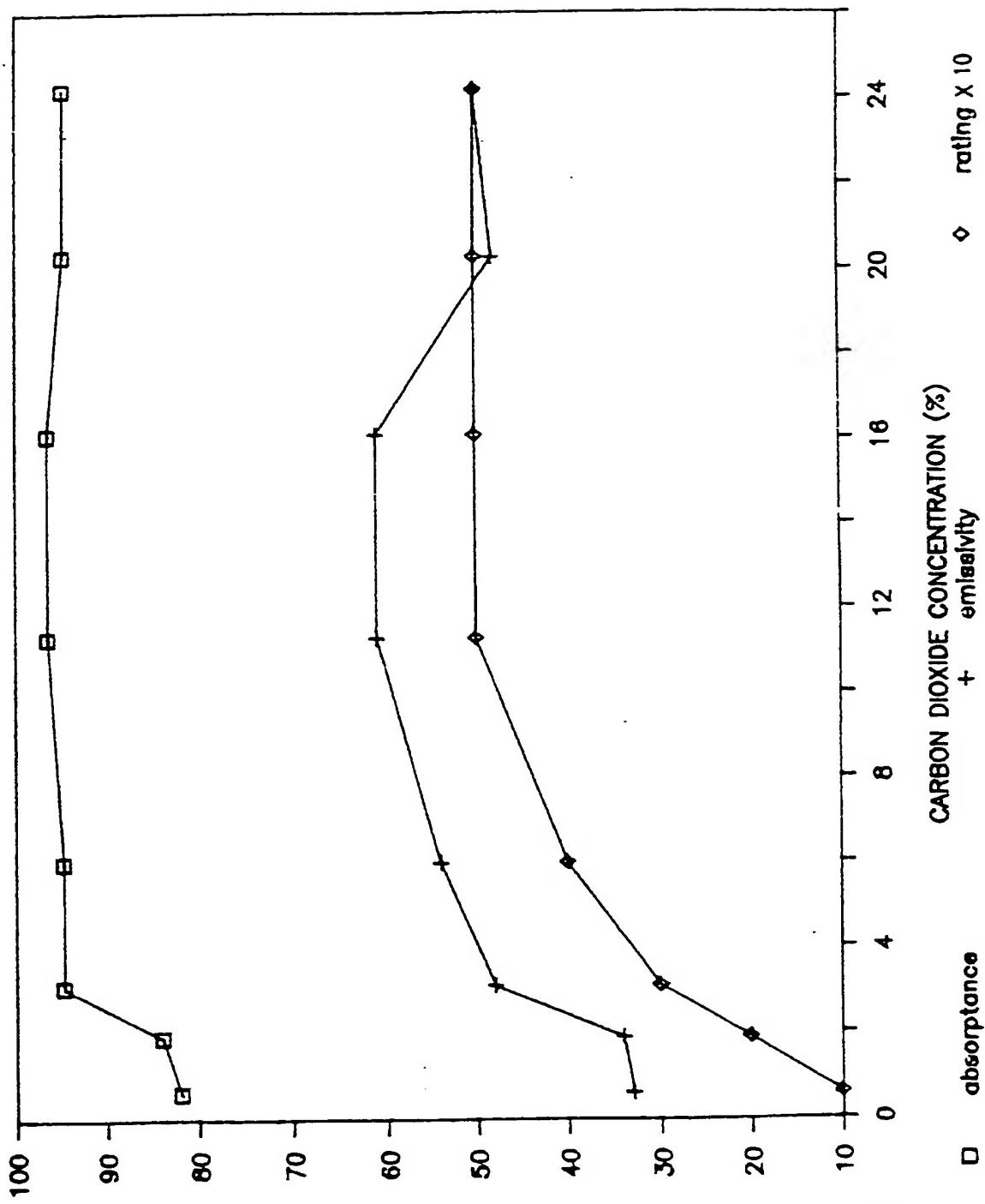
1 / 7



ABSORPTANCE (%), EMISSIVITY (%). RATING

FIG. 1

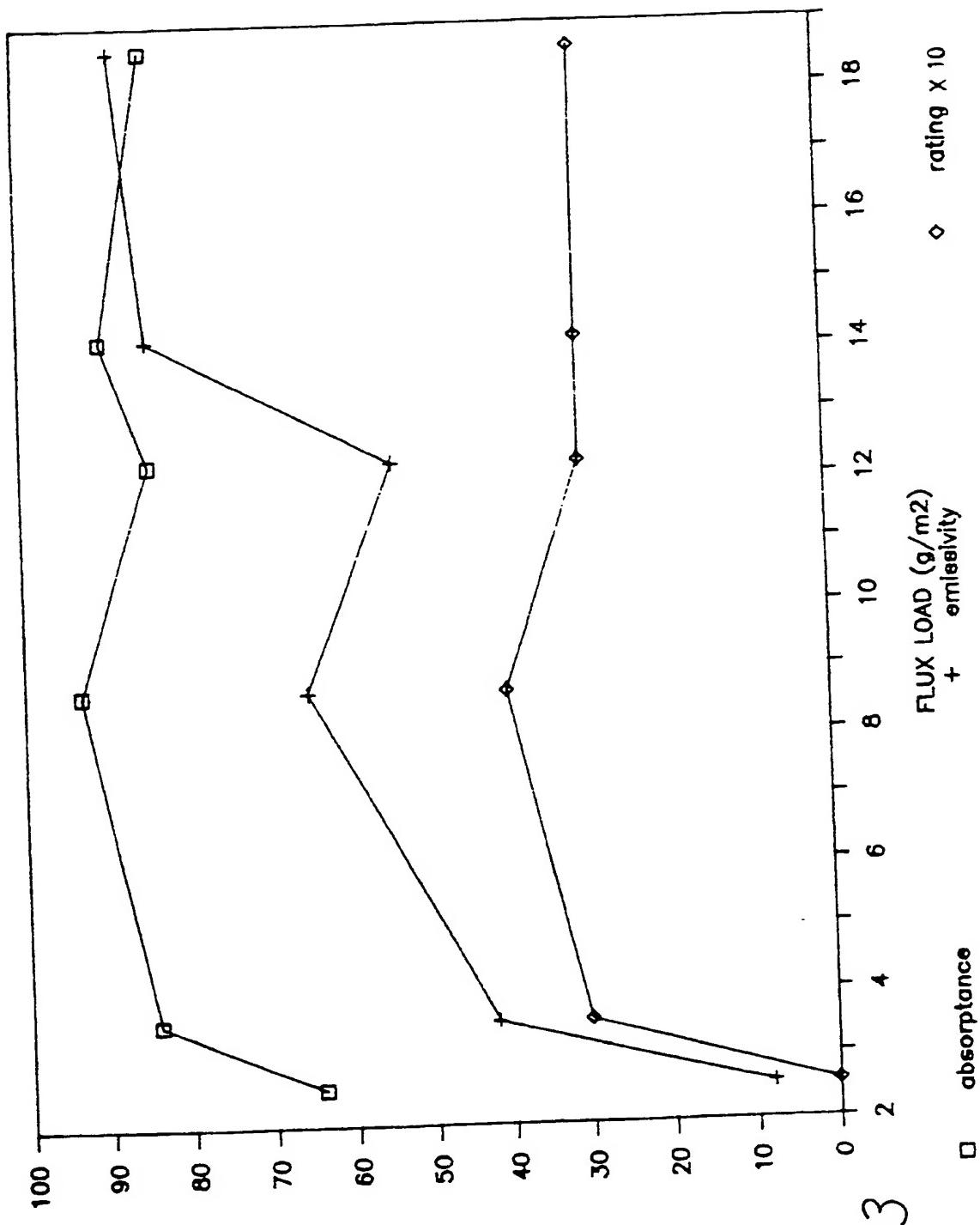
2/7



ABSORBANCE (%), EMISSIVITY (%), RATING

FIG.2

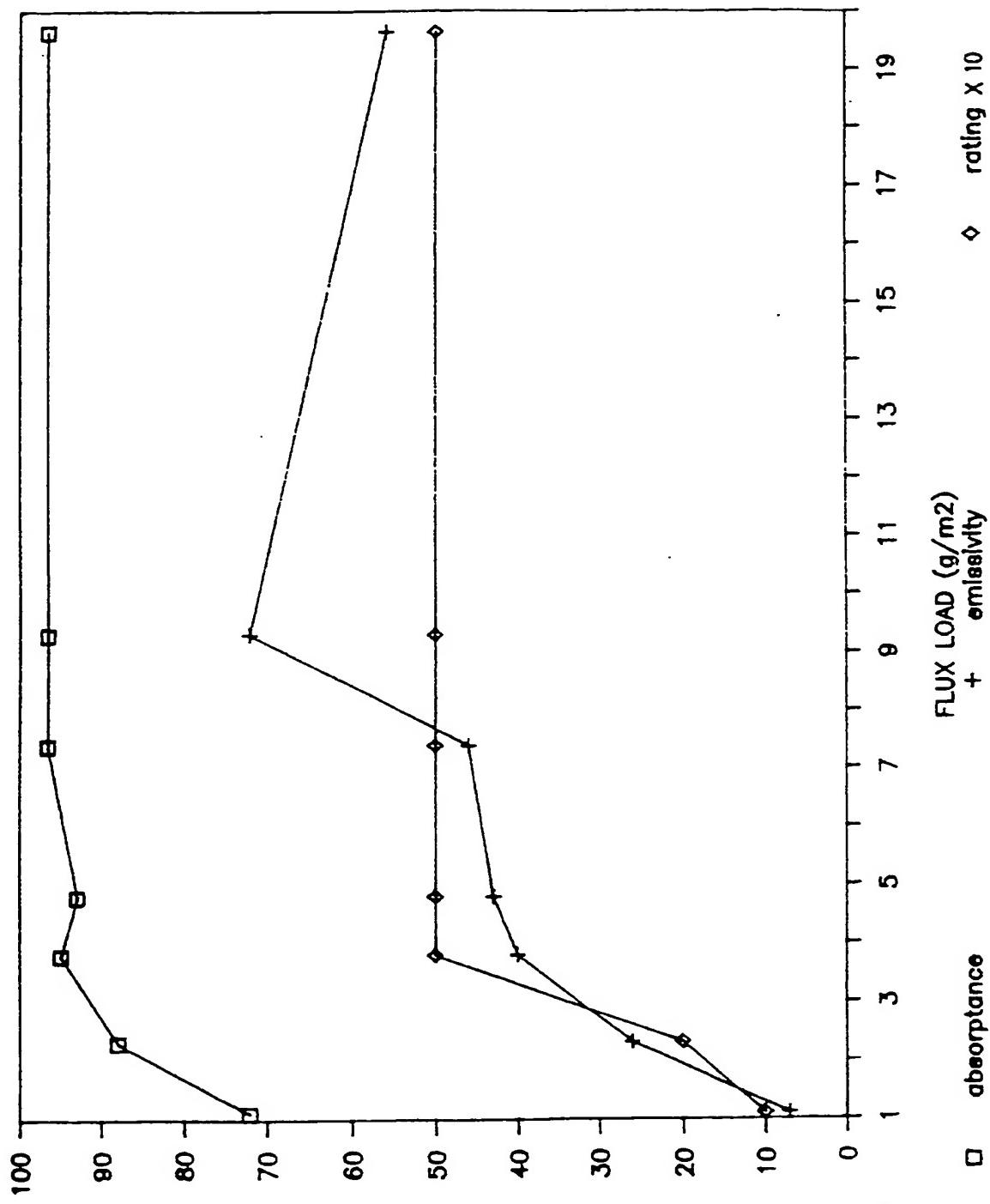
3/7



ABSORPTANCE (%), EMISSIVITY (%), RATING

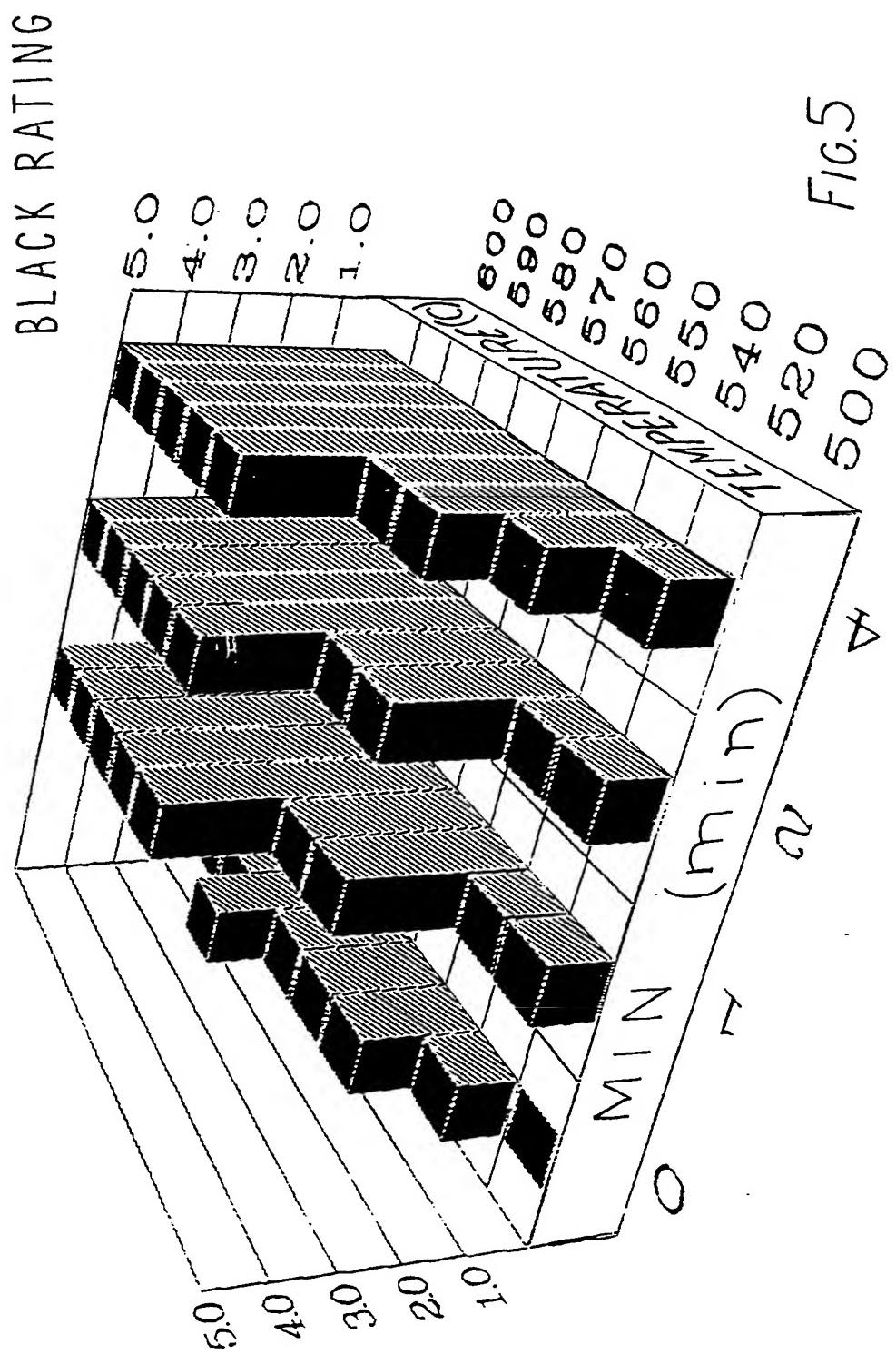
FIG. 3

FIG. 4



ABSORPTANCE (%), EMISSIVITY (%). RATING

5/7



PHASE 6.8-6.9 POSITION

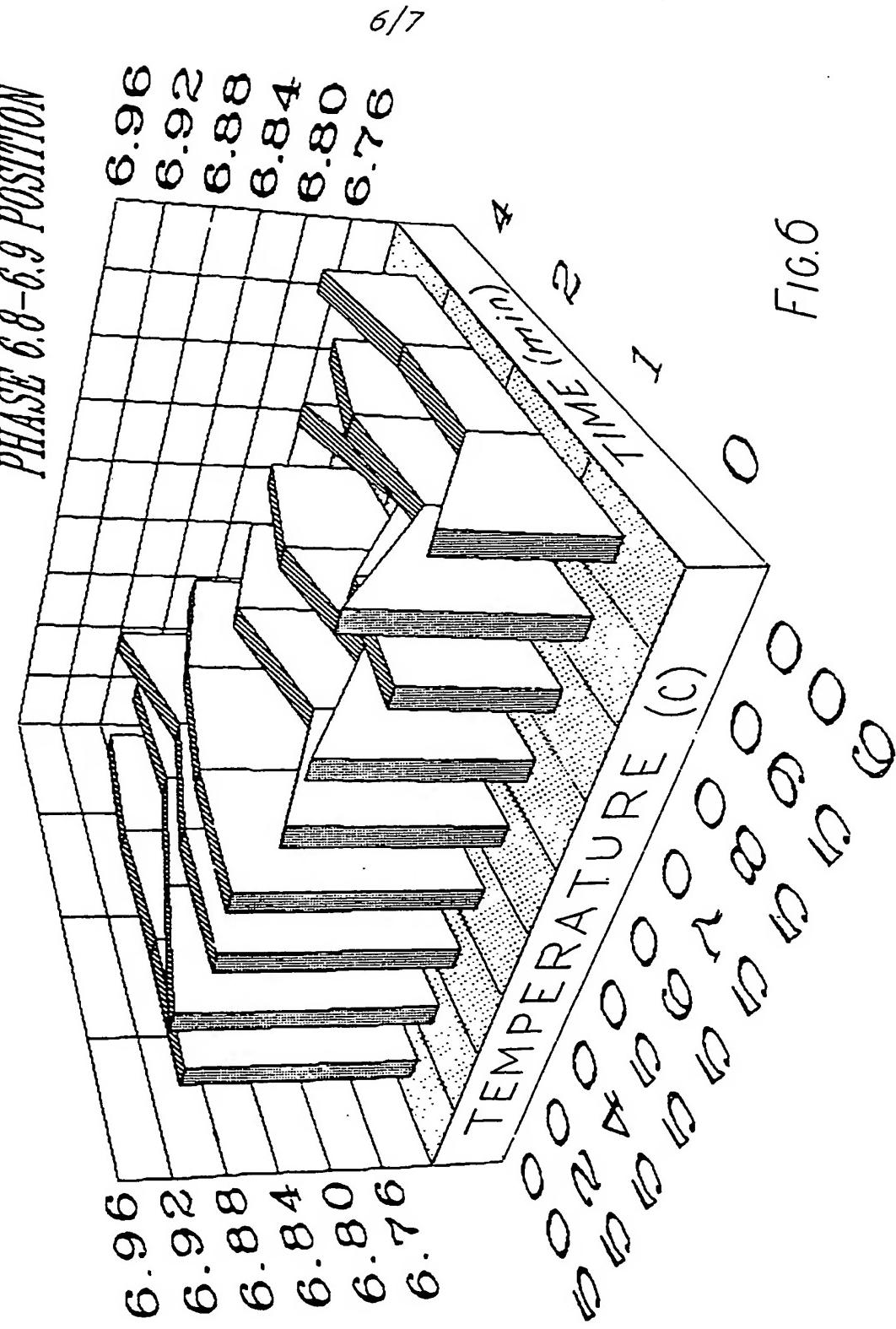
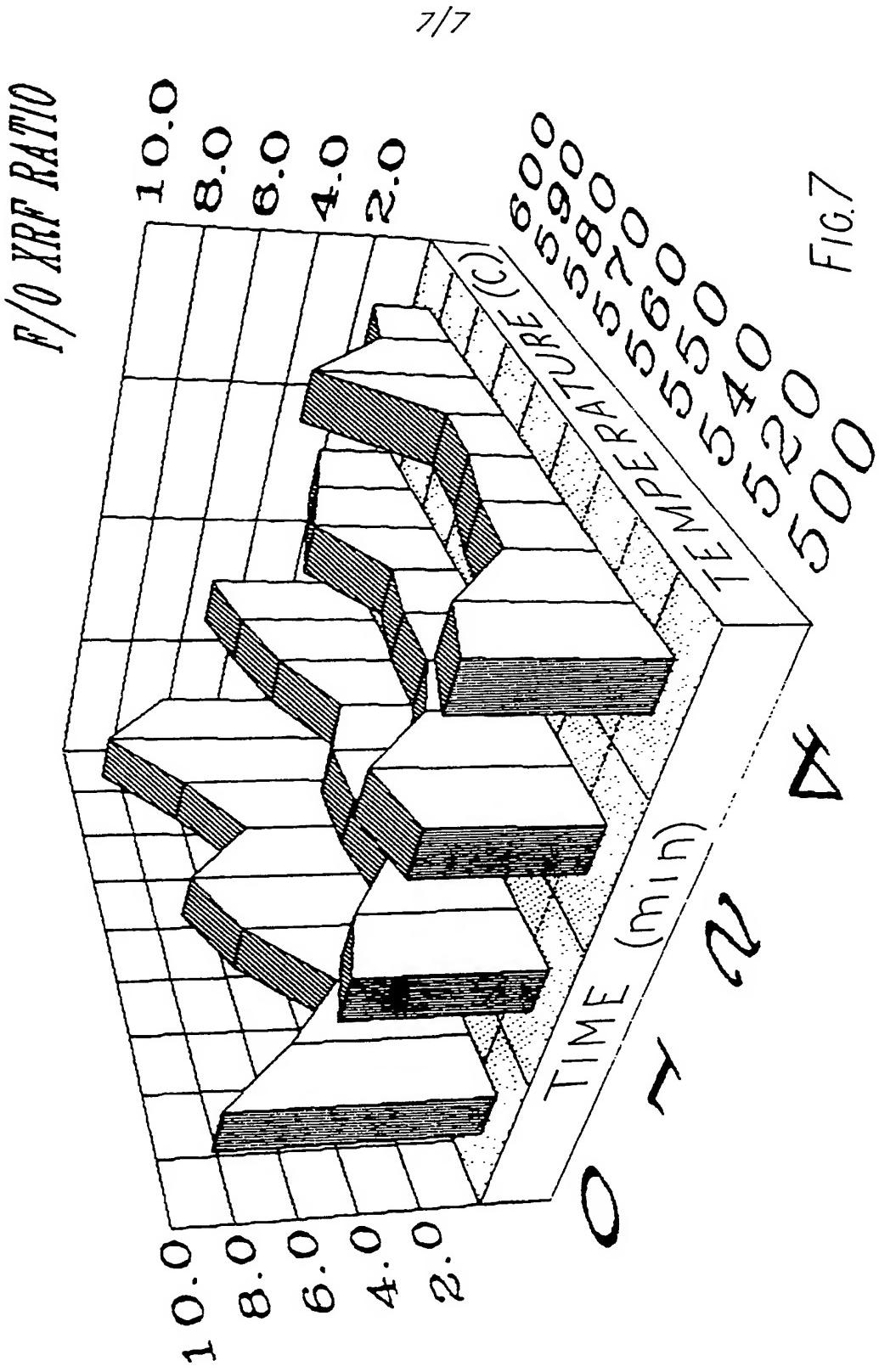


FIG.6



DARKENING ALUMINIUM WORKPIECES

This invention is concerned with the treatment of aluminium workpieces to darken their surface. An advantage which can be gained by the treatment is improved corrosion resistance, a matter of importance

5 e.g. in heat exchangers such as radiators. The treatment involves heating and can conveniently be performed in conjunction with brazing. The invention also extends to aluminium workpieces carrying a black adherent surface coating resulting from the
10 treatment.

When an aluminium workpiece is to be joined to another workpiece (generally, but not necessarily of aluminium) by means of a brazing alloy, a flux is used to remove any oxide film on the surfaces to be joined.

15 Brazing of aluminium can be performed in air, but a large amount of flux is required, and the strength of the brazed joints may be poor, particularly where the atmosphere is humid. For these reasons, brazing of aluminium is nowadays normally performed in an inert
20 atmosphere. Inert gas brazing reduces the flux levels required to achieve a successful braze, sometimes by as much as thirty times. Furthermore, at any flux loading, the quality of the braze is improved when the braze is made in an inert atmosphere. Thus for
25 example in the Nocolok brazing systems supplied by ourselves, which involve the use of a potassium/aluminium fluoride brazing flux, users are recommended to perform furnace brazing in an inert atmosphere.

One use of our Nocolok brazing system is described
30 in GB 1438955 and US 3951328. These patents teach the inclusion in the flux of a very small amount, such as $\frac{1}{2}\%$, of a conventional hydroxy ethyl cellulose thickening agent, which amount is however too small to lead to a desirable darkening of the surface during the brazing
35 operation.

Another use of our Nocolok brazing system is described in US 4723597. The brazing flux may contain carbon or other inorganic pigment. Brazing may be carried out in a non-oxidative gas, of which carbon dioxide is given as an example.

Our co-pending British Patent Application 8814056 filed 14 June 1988 describes a method of treating an aluminium workpiece by applying a coating comprising alkali metal and halogen values to the surface thereof, heating the coated workpiece in an inert atmosphere, bringing the heated workpiece into contact with an oxidizing atmosphere, maintaining the coated workpiece in contact with the oxidizing atmosphere at a temperature of generally at least 95% of the solidus temperature of the coating expressed in °K, and cooling the workpiece to ambient temperature. As oxidizing atmosphere there may be used air, oxygen, carbon dioxide, carbon monoxide or other oxygen-containing gases. The treatment results in a workpiece having improved corrosion resistance; where the oxidizing gas is carbon dioxide or carbon monoxide, the surface of the workpiece may also be darkened.

The present invention overlaps with our aforesaid co-pending British patent application. The present invention involves treating a surface of a workpiece with carbon and oxygen values, under conditions to darken the surface. The carbon and oxygen values may be provided by carbon oxides decomposition of selected carbonates and oxalates or in other ways. Treatment generally but not invariably results in a workpiece having improved corrosion resistance.

In one aspect this invention provides a method of treating an aluminium workpiece to darken a surface thereof which method comprises applying a coating comprising alkali metal and halogen values to the

surface, heating the coated workpiece in an inert atmosphere and bringing the heated workpiece into contact with a carbon oxide.

In another aspect the invention provides a method
5 of treating an aluminium workpiece to darken a surface thereof, which method comprises applying a coating comprising alkali metal and halogen values and containing at least 10% by weight of an carbon-oxygen containing compound and heating the coated workpiece in
10 an inert atmosphere to a temperature of from 95% of the solidus temperature of the coating expressed in °K up to the solidus temperature of the surface of the workpiece.

In yet another aspect, the invention provides an
15 aluminium workpiece, obtainable as a product of the aforesaid treatment, whose surface carries a black adherent coating comprising potassium, fluorine, aluminium, carbon and oxygen values, which coating preferably shows, on X-ray diffraction a peak at about
20 6.8A, \pm 0.1A and in X-ray fluorescence an F/O intensity ratio of from 1-14. This black adherent coating is advantageous because it:

- improves the appearance of the workpiece;
- eliminates the need for a separate painting
25 operation;
- is stable in air at temperatures up to 200°C; and for short exposures (< 30 mins) at temperatures up to 400°C;
- improves the thermal emissivity of the workpiece;
- can be applied to irregular shaped complicated
30 workpieces such as radiators; and
- increases resistance to corrosion, thereby extending the service life of the workpiece.

The term aluminium is intended to cover, not only
35 the pure metal, but also alloys containing a major

- proportion of aluminium. The term aluminium workpiece is intended to cover workpieces of aluminium and its alloys, and aluminium workpieces whose surfaces have been plated with zinc, nickel, or other metal, and then
- 5 heat treated at some stage to cause the metal on the surface to diffuse into the substrate of aluminium metal or alloy, and aluminized substrates such as steel which are covered with a layer of aluminium. As reported below, we have obtained good results on a wide
- 10 range of commercial aluminium alloys. The method is of particular interest in relation to brazing sheet, that is to say a sheet of an aluminium alloy having a relatively higher solidus coated with a layer of a brazing alloy having a relatively lower solidus.
- 15 Examples of suitable aluminium alloys include AA3003, 3003 bearing a diffused Zn layer, 3003 containing Mg, 4343, 4045, 4045 plus 1% Zn, 1050, 1050 bearing a diffused Zn layer, 7072, 9042, and AA No. 11, 12 and 13 brazing sheet.
- 20 Although the shape of the workpiece is not critical, the invention is of particular advantage in relation to workpieces of somewhat complex shape that are formed by brazing and in which complete surface coverage is otherwise somewhat difficult to achieve.
- 25 Heat exchangers are of particular interest in this context.
- Although generally good results are achieved with fluoride, chloride and iodide salts as coating, it is generally more convenient to use a fluoride or chloride.
- 30 It is particularly preferred to use complex potassium/aluminium fluorides such as those sold by us under the Trade Mark Nocolok. As described in USP 3951328, these are typically $KAlF_4$ or mixtures thereof with one or both of K_3AlF_6 and anhydrous K_2AlF_5 or $K_2AlF_5 \cdot H_2O$.
- 35 However, the effect on which this invention is based is

not confined to Nocolok fluxes, but is also observed when other commercially available halide brazing fluxes are used. The effect is also enhanced when additives, such as alkali and alkaline earth salts are added to
5 the flux. Such a flux containing LiF as the second alkali is described in EP 0091231. The presence of 2 to 7% LiF and 53 to 62% AlF₃ and 35 to 44% KF inherently depresses the solidus temperature to between 490 and 560°C. Another flux containing two alkali
10 metals is described in US 4670067, where the second alkali metal is present as CsF. It teaches that a composition of 62 mole % KF, from 2 to 74 mole % CsF, and 26 to 67% AlF₃ has a solidus temperature between 440 and 580°C. This composition can be expressed in
15 weight % as 18 to 59% KF, 5 to 55% CsF, and 27 to 36% AlF₃. It is of course necessary that a brazing flux be molten at the brazing temperature. Although this invention is not limited to brazing, it is nevertheless preferred that the aluminium workpiece be heated to a
20 temperature at which the halide salt is melted prior to or during exposure of the workpiece to the carbon oxide.

The amount of coating used should generally be in the range of 3 to 50 grams, preferably 5 to 15 grams, per square metre of workpiece surface. Although these
25 ranges are not critical, the beneficial effects are less apparent at application rates below 3g/m², and pale spots may become apparent at application rates above about 15 g/m². These rates are broadly in line with conventional rates for application of halide
30 brazing fluxes. It appears that the salt requirements for surface darkening according to this invention, and the flux requirements for brazing, are often of the same order.

Prior to coating, the workpiece may advantageously
35 be degreased with acetone, followed by dipping in KZ

solution which is a proprietary process (GB 2,140,461) to deposit a thin layer of metallic zinc on the surface of the workpiece; the zinc diffuses into the substrate on subsequent heating, or by an alkali dip (e.g. 2M

- 5 NaOH at 25°C for 2 minutes) followed by an acid dip (e.g. 8M HNO₃ at 25°C for 30 seconds.)

The coating of flux may be applied in conventional manner, either by dipping the workpiece in a solution or suspension, or by spraying or otherwise applying a 10 solution or suspension of the salt on the workpiece surface. It may be useful to apply the halide salt to the metal workpiece after it has been heated.

The coated workpiece is heated under an inert atmosphere. The use of argon or nitrogen is preferred, 15 but other inert gases provide acceptable alternatives. The atmosphere should preferably contain less than 1000 ppm free or combined oxygen (e.g. as air or water vapour). It may be advantageous to heat the workpiece under a reduced pressure and this may facilitate the 20 subsequent introduction of the carbon oxide.

The heated workpiece is then brought into contact with the carbon oxide, preferably carbon dioxide although carbon monoxide is possible. In order to achieve only darkening of the surface, the carbon 25 oxide content of the atmosphere surrounding the workpiece should be at least 0.1% by volume, preferably in the range 3 to 20% by volume, although the upper limit is by no means critical. For optimum corrosion resistance of the treated workpiece, carbon oxide levels should be kept down, preferably to from 5 to 15% 30 of the atmosphere, although improved corrosion resistance properties are still observable at higher carbon oxide concentrations. Overall, the carbon oxide partial pressure is preferably from 0.2 to 200 kPa.

35 Preferably, exposure of the workpiece to the

carbon oxide is effected in a controlled manner, preferably within a furnace e.g. a brazing furnace. Rather than simply use the carbon oxide to flush an inert atmosphere from the furnace, there may be

5 advantage in taking positive steps to bring the carbon oxide into contact with the workpiece. These steps may include heating the workpiece under vacuum; or alternatively directing the carbon oxide at the workpiece by means of pumps or jets.

10 On being exposed to the carbon oxide, the workpiece typically undergoes a rise in temperature, resulting from exothermic reaction involving the coating, the metal substrate, and the oxidizing atmosphere. The extent of this rise can be controlled

15 by controlling the rate and extent of the introduction of the carbon oxide. The coated workpiece is maintained in contact with the carbon oxide at a temperature of from 95% of the solidus temperature of the coating expressed in °K, up to the solidus

20 temperature of the workpiece. The temperature of the workpiece just prior to the introduction of the carbon oxide may be a little lower than this, so that the heating effect of the carbon oxide brings the workpiece into the desired temperature range. When the coating

25 has a solidus temperature of at least 560°C, the treatment temperature is preferably at least 550°C. When the coating has a solidus temperature below 560°C, the treatment temperature is preferably at least 520°. In general, the carbon oxide treatment is more

30 effective at temperatures at which the coating is permeable enough to permit diffusion of oxidant, e.g. at least 95% of the solidus temperature of the coating expressed in degrees Kelvin. (For example, 560°C is 833°K, of which 95% is 791°K or 518°C.)

35 Manifestly, the temperature of the workpiece prior

to the introduction of carbon oxide should not exceed the solidus temperature of the workpiece. It is however preferred that the local temperature at the surface of the workpiece be sufficiently high that the 5 coating, e.g. brazing flux, is melted and able to flow to provide uniform coverage over the entire surface, but less than the solidus temperature of the workpiece.

The workpiece is maintained in contact with the carbon oxide for a time sufficient to achieve the 10 desired surface darkening to grey or black. The time required for this varies with temperature, but is generally at least 15 seconds and preferably 30 seconds to 2 mins, although longer times up to e.g. 15 mins are not harmful. With workpieces of complex shape, it 15 needs to be borne in mind that the carbon oxide may take some time to reach the innermost recesses.

As noted above, the method of this invention may conveniently be performed in conjunction with brazing, in which case the coating may conveniently be a brazing 20 flux. In these circumstances it is preferred that the workpiece be heated to brazing temperature and maintained at that temperature for a time sufficient to effect brazing, under an inert atmosphere. The carbon oxide is introduced after brazing has been completed, 25 either at the brazing temperature, or more preferably at a somewhat lower temperature such that the workpiece is maintained at a temperature in the range 520°C to 550°C to the lower of the solidus temperature of the workpiece being processed, and 630°C, since superior 30 corrosion resistant properties can be obtained at temperatures in this range.

In an alternative technique, the coating applied to the workpiece contains a carbon-oxygen containing compound. Examples of suitable compounds are 35 carbohydrates such as sugars, starches, cellulose and

their derivatives, and oxalates and carbonates. The proportion of carbon-oxygen compound in the coating is at least 2% by weight and may be much higher e.g. up to 10% or even more, providing that the coating is
5 still able to perform its functions. When the carbon-oxygen compound is a carbohydrate, the proportion in the coating is preferably at least 10%. The coating containing the carbon-oxygen compound is applied to the surface of the workpiece at ambient temperature, prior
10 to heating. For example, sugar can be mixed into a solid flux, and a slurry in water prepared and applied to the workpiece. The coated workpiece is then heated in an inert atmosphere to a temperature of from 95% of the solidus temperature of the coating expressed in °K
15 up to the solidus temperature of the surface of the workpiece. At elevated temperature, the carbon-oxygen compound decomposes, and the carbonaceous residue darkens the surface of the workpiece. The workpiece is preferably maintained for 30 seconds to 4 minutes at a
20 temperature at least equal to the solidus of the flux.

Finally the workpiece is cooled to ambient temperature under conditions which are not critical. For example, the workpiece may be removed from a brazing or other furnace, at a temperature preferably
25 not exceeding 450°C, and allowed to cool in ambient air.

As a result of this treatment, an adherent grey or black layer is formed on the surface of the aluminium workpiece. The thickness of the layer depends on the
30 loading of the alkali metal/halogen coating and on the conditions of treatment, but is generally at least two microns and typically in the range 2 to 200 microns. When the coating is a potassium/aluminium fluoride, the film is formed of at least one complex of K with Al, O
35 and F.

The coating on workpieces (treated by the method) according to this invention has been examined by various techniques including X-ray diffraction, X-ray fluorescence and scanning electron microscopy. When 5 the initial coating is a potassium aluminium fluoride flux of the Nocolok type, it appears that a good black colour is the result of a two stage process of oxidation of the $KAlF_4$ component of the flux by carbon oxide (or by oxygen from decomposition of a carbon-oxygen compound in the coating). This oxidation 10 results first in an intermediate product of unknown constitution having an X-ray diffraction line at 6.9A. Further oxidation generates a different complex, also of unknown constitution, having an X-ray diffraction 15 line at 6.75 to 6.8A. This latter complex is preferred and is always present in the best black coatings obtained. Although it appears that there are two distinct complexes giving rise to two distinct lines, normally only one or the other shows on analysis. They 20 are however so close that they overlap when both "phase 6.8" and "phase 6.9" are present, appearing as one peak with a variable position reflecting their relative intensities. Depending on conditions, the combined peak generally appears in the range 6.75 to 6.90A, and 25 which will be referred to as $6.8 \pm 0.1A$. As a result of oxidation, the $KAlF_4$ peak at 3.08A reduces in intensity and is not visible in preferred products according to the invention.

As might be expected since an oxidation reaction 30 is involved, the oxygen intensity of the coating is raised when observed by X-ray fluorescence. The F/O X-ray fluorescence intensity ratio provides a convenient monitor of satisfactory treatment. In products according to the invention, this ratio is generally in 35. the range of 1 to 14, most usually 1 to 5; by contrast,

the F/O ratio in a normally brazed surface in an oxygen free atmosphere is generally greater than 20 and may be several hundred. Increases in the X-ray fluorescence intensities of both carbon and potassium are observed
5 in preferred products according to the invention, but may merely reflect more complete coverage of the underlying surface by the coating.

Scanning electron microscopy of workpieces treated at temperatures from 500 to 540°C shows obvious
10 evidence of protruding Al dendrites with (potassium aluminium fluoride) flux primarily in the valleys between the dendrites. This corresponds to conditions giving mottled black products. At temperatures of 560 and above, the whole surface typically appears covered
15 by a granular type of deposit, presumably complexes formed by oxidation of the potassium aluminium fluoride flux, though hexagonal crystal structure is not always apparent. In products treated at temperatures of 580°C and above, an acicular morphology begins to show.
20

References directed to the accompanying drawings in which:

- Figure 1 is a graph showing the effect of CO₂ concentration on absorptance, emissivity and blackness rating for an AA Number 12 brazing sheet heat treated at 565°C for 2 minutes using 4 g/m² Nocolok flux.
- Figure 2 is a graph showing the effect of CO₂ concentration of absorptance, emissivity and blackness rating for an AA Number 12 brazing sheet heat treated at 565°C for 2 minutes using 12 g/m² Nocolok flux.
- 30 - Figure 3 is a graph showing the effect of flux load on absorptance, emissivity and blackness rating for an AA Number 12 brazing sheet heat treated at 565°C for 2 minutes in 3% CO₂.
- Figure 4 is a graph showing the effect of flux load and absorptance, emissivity and blackness rating

for an AA Number 12 brazing sheet heat treated at 565°C for 2 minutes in 24% CO₂.

5 - Figure 5 is 3-D representation showing the effects of time and temperature on the black rating of CO₂-treated AA Number 12 brazing sheet, where time (min) refers to the length of time the sample is exposed to CO₂ at the indicated temperature, and temperature refers to the temperature at which the CO₂ is introduced.

10 - Figure 6 is a 3-D representation showing the effects of time and temperature on the X-ray diffraction line position of "phase 6.8 - 6.9" for CO₂-treated AA Number 12 brazing sheet surface.

15 - Figure 7 is a 3D representation showing the effects of time and temperature on the fluorine/oxygen X-ray fluorescence ratio for CO₂ treated AA Number 12 brazing sheet.

EXPERIMENTAL

Except where indicated the tests described in the Examples were carried out with 3.16 cm o/d disks made from standard AA Number 12 brazing sheet or AA1050 sheet 0.55 mm thick. A potassium fluoaluminate flux sold under the Trade Mark Nocolok flux 100, was employed. After degreasing with acetone, a controlled amount of Nocolok flux was sprayed on only one side of the aluminium disks. Both nitrogen and carbon dioxide supplied for brazing and post-brazing experiments had dew points corresponding to -54°C or less.

20 A stainless steel furnace with a total volume of 4.83 L was employed for brazing simulation experiments.
25 All gases were introduced in the system from the door end and released from the opposite hot end of the furnace.

30 The temperature of the test pieces was monitored with a 0.5 mm o/d K-type stainless steel thermocouple placed in contact with the center of the samples'

unfluxed underside. The specimens were all heat-treated while sitting horizontally in the furnace.

Prior to brazing simulation, the furnace containing the sample to be brazed was purged for 10 to 5 15 minutes with nitrogen flowing at a rate of 4 L/min. This purging step brought the sample temperature to 200°C thus dehydrating the flux as well as removing moisture and oxygen from the brazing atmosphere giving a dew point of less than -50°C. After completion of 10 nitrogen purge the aluminium specimen was transferred into the hot section of the furnace which was pre-set and maintained at 660°C. The temperature of the sample was increased to 605°C and then gradually lowered to the desired treatment temperature and this temperature 15 maintained for the desired period of time. The temperature of the sample was subsequently lowered to 400°C or less in the nitrogen-carbon dioxide gas mixture and finally the sample was removed into the ambient atmosphere.

20 Static pressurized nitrogen atmosphere was employed during brazing and post-brazing treatments. Nitrogen pressure in the furnace was adjusted to 70 kPa while the samples were being heated. Then just prior to introducing carbon dioxide the nitrogen pressure was 25 reduced to 7 kPa.

Treatment was carried out at given temperatures on the cooling side of the brazing cycle with the introduction of carbon dioxide in the system up to the desired pressure which was attained within 10 to 15 30 seconds.

The absorptance of the treated surfaces was measured with an Willey Alpha Meter model 2150. The emissivity of the surfaces was quantified with a McDonald Emissometer model 2145.

35 A good black surface is characterized by high

absorptance (Alpha) and high emissivity value.

In addition to the above measurements, a 0 to 5 rating was given to the treated specimens where 0 corresponds to no black at all and 5 to a uniform black coating. The intermediate values correspond to various shades of grey. The uniformity of the black coating was also taken into consideration in this arbitrary rating scale.

10

EXAMPLE 1

Effect of CO₂ concentration on the formation of black deposits on AA Number 12 brazing sheet.

The process was carried out at 565°C for 2 minutes on the cooling side of the brazing cycle using various concentrations of CO₂ in the brazing furnace. The effect of CO₂ on AA Number 12 brazing sheet blackness was evaluated for 4 g/m² and 12 g/m² Nocolok flux.

Results are set out graphically in Figures 1 and 2. These figures confirm that, if uniform, any surface with at least 90% absorptance and at least 50% emissivity can be regarded as having an acceptable black coating. It is apparent that, at both levels of flux loading, a carbon dioxide concentration of at least 3%, and preferably at least 5%, by volume is effective to provide a good black surface. Above these levels, the carbon dioxide concentration is not critical so far as the black rating is concerned. Other results (not reported here) show that the carbon dioxide concentration should preferably be in the range of 3 to 15% for optimum corrosion resistance.

EXAMPLE 2

Process carried out with 0.6% V/V Carbon Dioxide.

A serpentine condenser segment was fabricated from eight AA1050 extruded tube sections and seven rows of

AA4045/AA3003/AA4045 brazing fin material. The overall dimensions of this unit were 20 cm x 17 cm x 2 cm.

This assembly was vapour degreased and spray coated with a flux slurry composed of 16 w/w% Nocolok 5 flux in isopropyl alcohol. After drying at 200°C in ambient air for 10 minutes the flux load was evaluated and corresponded to 10 g/m².

The fluxed assembly was placed in a brazing furnace which had a total volume of 1.1 m³. The 10 serpentine condenser was heated in ambient air to 200°C and then the furnace atmosphere was evacuated to less than 6.5 Pa. The furnace was subsequently pressurized with nitrogen up to 35 kPa above atmospheric pressure. This completed the purging of the furnace atmosphere 15 giving less than 120 ppm H₂O and less than 400 ppm O₂ in the furnace.

The aluminum assembly was heated from 200°C to 600°C in around 10 minutes giving a heating rate of 20°C/min between 500°C and 600°C. The unit was cooled 20 to 576°C at 26°C/min in 35 kPa nitrogen. At 576°C, the pressure in the furnace was reduced to 7 kPa nitrogen and then a gas mixture containing 24 v/v% CO₂ in nitrogen was introduced into the system to give a total pressure of 10 kPa within 20 seconds.

25 The final carbon dioxide concentration in the furnace corresponded to 0.6 v/v%. This resulted in a gradual increase of the temperature of the brazed assembly which attained 590°C during the 2 minutes reaction time with CO₂.

30 Two minutes after the initial introduction of CO₂ in the furnace the temperature of the Blackolok treated unit was dropped to 400°C at a rate of around 30°C/min.

At 500°C during cooling, the furnace was evacuated to less than 13 Pa and back filled with nitrogen. The 35 furnace door was opened at 400°C and the unit quickly

removed from the furnace and cooled to room temperature to minimize oxidation of the carbonaceous layer.

A silver and gray brazed unit was obtained after this treatment with 0.6 v/v% carbon dioxide. Even this 5 low concentration of carbon dioxide produced a gray unit that has never been observed under normal inert atmosphere Nocolok brazing conditions. The lustre of the unit was also reduced by this CO₂ treatment.

10

EXAMPLE 3

Effect of flux load on the formation of black coating on AA Number 12 brazing sheet.

The process was applied to AA Number 12 brazing sheet coated with various amounts of Nocolok 100 flux 15 using a 2 minute temperature soak at 565°C. The reaction was carried out with 3% CO₂ and 24% CO₂.

Results are presented graphically in Figures 3 and 4, where again an absorptance of at least 90% and an emissivity of at least 50% are good indications of an acceptable black coating. These figures clearly show 20 that a minimum flux load of 3 to 4 g/m² is required to achieve a satisfactory black deposit. Above these levels, black rating is not significantly dependent upon flux load. However, an excessive amount of flux 25 led to the formation of flux crystals on the brazed surface thus blocking CO₂ access to the underlying Al-flux interface. This led to the formation of small but distinct white spots on the surfaces. To avoid this, the flux loading is preferably in the range 5 - 15 g/m².

30

EXAMPLE 4

Effect of time and temperature on formation of black coatings on AA Number 12 brazing sheet.

The effect of temperature on the process was 35 measured using 8 ± 1.5 g/m² flux load and 24% CO₂. The

AA Number 12 brazing sheet substrates were heat-treated in CO₂ at selected temperatures ranging from 500°C to 600°C on the cooling side of the brazing cycle for 0 - 4 minutes holds. (A 0 minute hold indicates that the CO₂ was introduced at a particular temperature during the cooling phase, but without delaying the cooling.)

The results are set out graphically in Figure 5. These show that for optimum black rating, a temperature of at least 560°C for a hold time of at least half a minute is required. Positive though inferior results were obtained at temperatures of at least 540°C. Other tests (not reported) have shown that heating for longer periods up to 15 minutes at 545 to 550°C still does not give rise to optimum black ratings. This suggests that temperature, not time, is the prime factor affecting the black rating. If the flux does not melt and flow during the treatment with carbon dioxide, a uniform black coating is not obtained.

Tests were also performed on AA Number 12 brazing sheet and AA1050 alloy at temperatures up to 640°C. Although good black ratings were obtained, the coatings on number 12 brazing sheet above 580°C exhibited very poor adhesion. This test demonstrated that treatment can be successfully applied at temperatures as high as 640°C. However, the adhesion of the oxyfluoride layer is determined by the temperature at which the aluminium substrate surface melts. Optimum results are obtained when the temperature of the workpiece is maintained below the solidus of the metal while the oxidation reaction takes place.

Further coupons, treated under the conditions of this example, were subjected to corrosion testing. It was determined that improved corrosion resistance was obtained by CO₂ treatment, generally similar improvements being apparent at all temperatures from

500 to 600°C and at all treatment times from 0 to 4 minutes.

EXAMPLE 5

5 Treatment applied to various aluminium alloys.

Selected aluminium alloys were treated to assess the effectiveness of the process for alloys with higher melting points than AA Number 12 brazing sheet. The alloys were all heated to 605°C in N₂ and cooled to 10 570°C in N₂ as well. Treatment was carried out at 570°C for 2 minutes in 24% CO₂ by volume. All the alloys tested exhibited rather uniform black coatings and acceptable adhesion. The alloys were:

| | Alloy | Flux Load (g/m ²) |
|----|-------------------------------|-------------------------------|
| 15 | a) AA3003 + 5% Zn + 0.002% In | 6.9 |
| | b) AA3003 + 5% Zn + 0.04% In | 7.4 |
| | c) AA3003 (1.03% Mn) | 8.3 |
| | d) AA3003 + 0.87% Si | 7.9 |
| | e) AA3003 + 0.8% Mg | 8.7 |
| 20 | f) 0.07 Mn + 1.15% Si | 9.7 |
| | g) AA1100 | 9.1 |
| | h) AA2036 (2 - 3% Cu) | 8.5 |

In another experiment, sections of an AA1050 extruded serpentine tube previously zincated by the 25 proprietary KZ process (GB 2,140,461) were coated with 2.7 to 33.8 g/m² Nocolok flux and treated in 6% by volume CO₂ at 570°C for 1 minute on the cooling side of the brazing cycle. The tube sections were coated with 17 g/m² Zn.

30 The results showed that at least 5 g/m² flux, and preferably about 7 to 14 g/m² flux, was required to produce acceptable uniform black coatings. Flux loadings exceeding about 20 g/m² had a negative impact on the black finish. However, the amount of plated 35 zinc is likely to affect the flux load range required

for optimum black ratings.

EXAMPLE 6

Exposure to air at various temperatures

5 The following tests were carried out in order to determine the affect of the introduction of air in the brazing furnace, as part of the cooling cycle, on treated surfaces.

10 The treatment was applied to AA Number 12 brazing sheet as described previously. Then following a 2 minute soak at 570°C in 24% CO₂, the CO₂/N₂ pressure was reduced from 40 kPa to 7 kPa while the sample was cooled down at a rate of about 40°C/minute. During this cooling step, without temperature hold, 70 kPa dry air was introduced into the brazing furnace at either 15 525°C or 450°C.

20 Some discolouration was observed on the surface exposed to dry air at 525°C. No change was noted on the black specimen that had been in contact with air at 450°C during the cooling step. Thus, unless the cooling rate is very slow, it is safe to expose a treated workpiece to air at 450°C or lower on the cooling side of the brazing cycle.

25 In another experiment, various coupons which had been brazed, subjected to CO₂ treatment as previously and cooled to ambient temperature in CO₂, were heated to various temperatures ranging from 400°C to 570°C in ambient air at atmospheric pressure. The selected temperature was maintained for 1 minute and then the 30 sample was cooled down to room temperature.

35 No change in colour was observed on the sample heat treated in ambient air at 400°C. There was some degradation of the black coating at 490°C. It is concluded that the products of this invention can be heated in air to temperatures not exceeding 450°C for a short time i.e. < 30 mins, without substantial damage.

EXAMPLE 7

Process applied to a specimen previously brazed in inert atmosphere.

A piece of AA Number 12 brazing sheet was fluxed with 10 g/m² Nocolok 100 flux and heated to 605°C in N₂ atmosphere. The sample was then cooled down to 200°C in the inert atmosphere without any temperature hold. After 30 minutes at 200°C in dry flowing N₂, the brazed sample was reheated to 570°C, at which temperature it was allowed to react with 24% by volume CO₂ for 2 minutes. After cooling to 400°C in the CO₂/N₂ atmosphere, the coupon was taken out of the furnace. The product had an excellent adherent black surface.

In another experiment, the brazed sample was cooled to ambient temperature in N₂ and then exposed to ambient air for 24 hours at 25°C, before being heated in N₂ to 570°C as before. Again, the treated product had an excellent adherent black surface.

COMPARATIVE EXAMPLE 8

All carbon dioxide brazing cycles.

After purging the furnace atmosphere with nitrogen, various Nocolok fluxed alloys were heated in 36% by volume CO₂ to 580°C and then allowed to cool to 400°C before being removed from the brazing furnace. The treatment produced grey to black coatings, but the colour was not uniform. Increasing the amount of flux from 10 to 20 g/m² did not improve the uniformity of the flux layer, even though a darker coating was obtained.

Furthermore, the brazing capability of AA Number 12 brazing sheet is completely suppressed in an all carbon dioxide brazing cycle. The alloys treated were:

| | Alloy | Flux Load (g/m ²) |
|----|-------------------------|-------------------------------|
| a) | AA No. 12 brazing sheet | 10 |
| b) | AA No. 12 brazing sheet | 20 |
| c) | AA1050 | 10 |
| d) | AA3003 + 0.8% Mg | 10 |
| e) | AA4104 (1.4% Mg) | 10 |

EXAMPLE 9

Brazing using a mixture of flux and sugar.

Around 10 g/m² of a 50/50 by weight mixture of Nocolok 100 flux and finely ground commercial sugar
5 was applied to a sample of AA Number 12 brazing sheet. The sample was heated to 610°C in argon and quenched down to 300°C in argon.

A black coating with improved corrosion resistance was obtained, and there were no lumps on the surface
10 after brazing. X-ray diffraction results on the coating were as follows:

| | Wavelength (Angstroms) | Intensity (cps) |
|----|---|-----------------|
| | 6.9 | 30 |
| 15 | 3.25 | 0 |
| | 3.09 (KAlF ₄) | 580 |
| | 2.90 (K ₃ AlF ₆) | 0 |
| | 1.43 (Al) | 400 |

20 EXAMPLE 10

Brazing using a mixture of flux and sodium oxalate

36 g/m² of Nocolok flux containing 17% w/w sodium oxalate was applied to a sample of AA No. 12 brazing sheet. The sample was heated to 600°C in nitrogen and
25 cooled to below 400°C in nitrogen.

A non-uniform black coating was obtained. X-ray fluorescence and diffraction results obtained on the coating were as follows:

| | | |
|----|-----------|--------------|
| 30 | XRF data: | K = 135 kcps |
| | Si = | 20 kcps |
| | Al = | 6 kcps |
| | F = | 23 kcps |
| | C = | 2 kcps |
| 35 | C = | 0.1 kcps |

| | | | | |
|-----------|--------------|----------|---|---------|
| XRD data: | Phase 6.8 | (6.8 A) | = | 610 cps |
| | 3.25 | (3.24A) | = | 80 |
| | Si | (3.15A) | = | 370 |
| 5 | K_3AlF_6 | (2.99A) | = | --- |
| | $KAIF_4$ | (3.08A) | = | 20 |
| | K_2NaAlF_6 | (2.87A) | = | 1360 |
| | K_2LiAlF_6 | (4.57A) | = | --- |
| | Al | (1.432A) | = | 1760 |

10

EXAMPLE 11

Example 4 was concerned with treatment at various times and temperatures and reported on the black ratings of products so obtained (illustrated in Figure 5). This example concerns other properties of the products obtained under the conditions of Example 4.

Figure 6 is a 3-D representation of the effect of time and temperature on the wavelength of the X-ray diffraction line at about 6.8A. It is believed that there are two distinct line positions, which are however so close that they overlap when both are present, appearing as one peak with a variable position reflecting their relative intensities. "Phase 6.9" is believed to be an intermediate complex produced by partial oxidation of $KAIF_4$. "Phase 6.8" is the final complex produced by oxidation of $KAIF_4$ and is always present in preferred products according to the invention. From Figure 6, it can be seen that "Phase 6.8" predominates at treatment temperatures of 560 to 600°C, but that "Phase 6.9" is present in products treated at temperatures from 500 to 550°C.

Figure 7 is a similar 3-D representation of the fluorine/oxygen intensity ratio obtained by X-ray fluorescence of the treated products. It can be seen that the ratio is not very temperature dependent, but tends to reduce with increasing treatment time, and is in all cases within the range of 1 to 14.

CLAIMS

1. A method of treating an aluminium workpiece to darken a surface thereof which method comprises applying a coating comprising alkali metal and halogen values to the surface, heating the coated workpiece in an inert atmosphere and bringing the heated workpiece into contact with a carbon oxide.
2. A method as claimed in claim 1, wherein the heated workpiece is maintained in contact with the carbon oxide at a temperature of from 95% of the solidus temperature of the coating expressed in °K up to the solidus temperature of the workpiece.
3. A method as claimed in claim 2, wherein the temperature is from 560 - 640°C.
4. A method as claimed in any one of claims 1 to 3, wherein the workpiece is maintained in contact with the carbon oxide for from 5 seconds - 15 minutes.
5. A method as claimed in any one of claims 1 to 4, wherein the coating is applied at a dry weight of 3 - 25 g/m² of surface.
6. A method as claimed in any one of claims 1 to 5, wherein the coating comprises a potassium/aluminium fluoride brazing flux.
7. A method as claimed in any one of claims 1 to 6, wherein the heated workpiece is maintained in contact with an atmosphere containing from 0.1 - 50% by volume of carbon oxide.
8. A method as claimed in any one of claims 1 to 7 performed in conjunction with brazing, wherein the coating is a brazing flux, the workpiece is heated in an inert atmosphere to a temperature to effect brazing and is thereafter brought into contact with the carbon oxide.
9. A method of treating an aluminium workpiece to darken a surface thereof, which method comprises

- applying a coating comprising alkali metal and halogen values and containing at least 2% by weight of a carbon-oxygen containing compound and heating the coated workpiece in an inert atmosphere to a
- 5 temperature of from 95% of the solidus temperature of the coating expressed in °K up to the solidus temperature of the workpiece.
- 10 10. A method as claimed in any one of claims 1 to 9, wherein the workpiece is a heat exchanger.
11. An aluminium workpiece whose surface carries a black adherent coating comprising potassium, fluorine, aluminium carbon and oxygen values.
12. An aluminium workpiece as claimed in claim 11, wherein the black adherent coating shows, on X-ray
- 15 diffraction, a peak at $6.8 \pm 0.1\text{\AA}$, and in X-ray fluorescence an F/O intensity ratio of from 1-14.

20

25

30

35

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)